Gelcasting SiAlON Radomes

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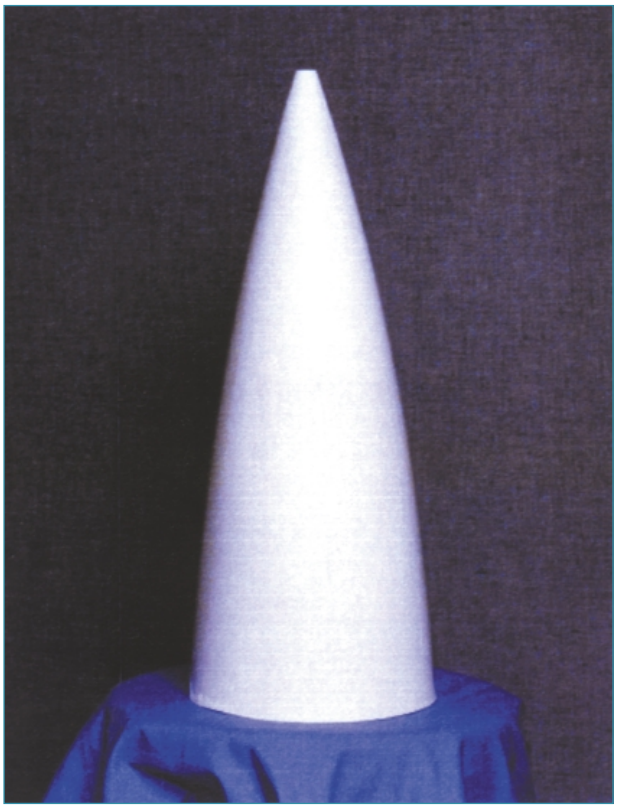

Green gelcast radome.

Full-sized SiAlON radomes were fabricated using aqueous gelcasting with water-resistant AlN powder and mixing procedures that allowed achievement of high slurry density and liquid desiccant drying.

During the 1980s, General Dynamics-Pomona developed an improved radome material[1] that had properties superior to the standard radome material of the time, i.e., Corning Pyroceram®. The General Dynamics material was known as GD-1 and consisted of a β-SiAlON phase (Fig. 1). The material had the nominal composition $Si_{6-z}Al_zO_zN_{8-z}$, where $z \leq 2$. This material was isostructural with β-Si_3N_4 and tended toward some of its properties (Table I).[2] GD-1 was optimized for high-temperature dielectric properties, especially low loss tangent at radar frequencies, while it retained reasonable strength, hardness and thermal shock properties.

A nonaqueous slip-casting process was developed at General Dynamics to produce GD-1 radomes. Nonaqueous processing was required to accommodate the AlN powder in the starting materials. Although full-scale monolithic radomes were produced using this method, cracking and warping during the drying process consistently kept yields low. Consequently, despite the desirable material properties, the material-processing difficulties forced General Dynamics to abandon radomes based on the GD-1 formulation.

In 1995, GD-1 fabrication was revisited in a collaborative effort between Hughes Missile Systems Co.-Tuscon (the successor to General Dynamics-Pomona) and Oak Ridge National Laboratory. Gelcasting was selected as the forming method.

Gelcasting is a slurry-based ceramic-forming process. A slurry comprising ceramic powder and a monomer solution is poured into a mold, polymerized in situ to immobilize the particles in the gelled part, removed from the mold while still wet, then dried and fired (Fig. 2). Details of the gelcasting process are given elsewhere.[3]

Gelcasting Raw Materials

The raw materials selected to develop the 1985 GD-1 formulation were based primarily

on their high purity and not on their ceramic-processing properties. This may have contributed to the difficulties encountered in slip casting these materials. By 1995, ceramic powders had evolved significantly and could be selected for high purity and processability. Hence, several of the raw materials selected for radome production were changed (Table II).

Original GD-1 slip casting was done in a nonaqueous solvent to prevent hydrolysis of the AlN component of the slurry. By 1995, a water-processable AlN (AlN-WR100, ART Inc., Buffalo, N.Y.) had become available and was selected for the gelcasting trials. Initial trials to determine the processing envelope for the water-resistant AlN showed that, although AlN-WR100 could be processed in water, even water-resistant AlN could react with water under certain conditions.

- Prolonged mixing of AlN-WR100 in water had to be avoided. This was demonstrated when a jar mill exploded while being mixed over a weekend. The water-resistant coating provided protection to the AlN powder for 24 h, as demonstrated when the slurry was mixed overnight. However, 72 h was too long. The AlN reacted with the water in the slurry to form $Al(OH)_3$ and NH_3 gas, which built up extreme pressures and blew the cap off the polyethylene mixing jar. Thus, it was decided that the AlN fraction of the slurry would be the last component added and that it would be mixed for as short a time as possible after addition.
- AlN-WR100 was resistant to attack by water at ambient temperature but not at elevated temperature. The original gel-casting trials with AlN-WR100 gelled the slurry at 50°C. When the mold was opened, a strong ammonia smell was noted and the slurry had turned to concrete. The AlN again had reacted with water to form a cementitious $Al(OH)_3$ phase, which had to be chipped out of the mold with a chisel. Thus, it was decided that the GD-1 formulation would be gelled at ambient temperature.

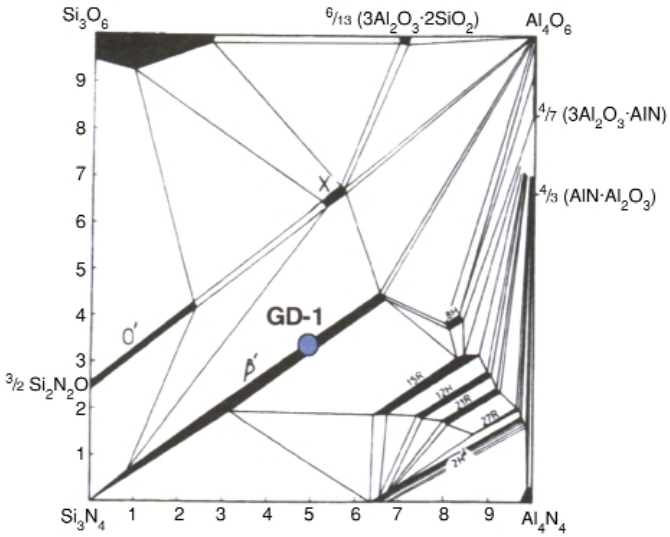

Fig. 1. Quaternary phase diagram showing location of GD-1 composition.

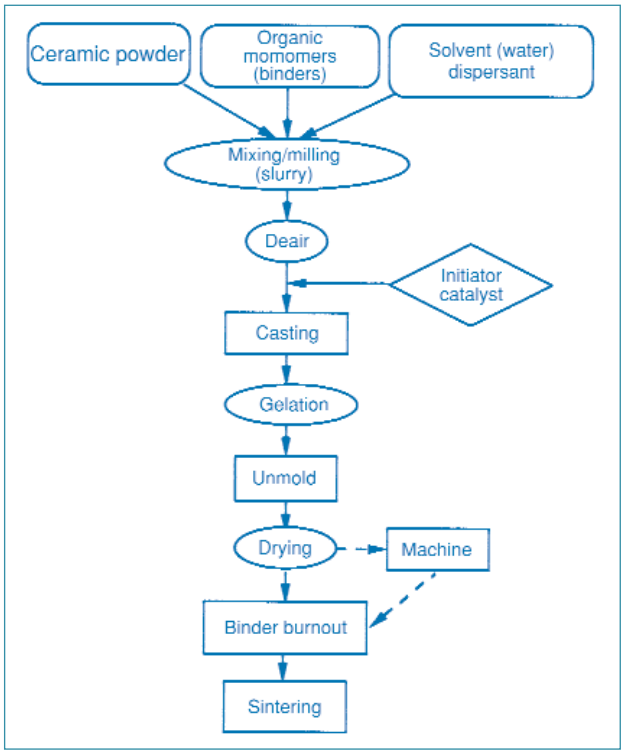

Fig. 2. Gelcast processing is similar to other ceramic processes, such as slip casting and spray drying.

Gelcasting Monomer, Dispersant and Defoamer Selection

Because the radome was large (8.5 in. (1.6 cm) diameter at the base by 23 in. (58 cm) tall in the green state) and had a thin wall (0.25 in. (0.64 cm)), a gel system was used that was as stiff and strong as possible. The monomer system MAM–NVP– MBAM (3:3:1, 20 wt% total monomer in solution) was chosen based on a previous study of gel strength and stiffness.[3]

ART recommended Emphos CS1361 (Witco Chemical, Houston) as dispersant for the AlN100WR, which also required use of Foamaster VF (Witco Organics Div., Houston) as a defoamer for the foam caused by the Emphos CS1361.

Dolapix PC33 (Zschimmer and Schwarz, Berlin) was used as the main dispersant for Si_3N_4 and Al_2O_3. The efficacy of

Table I. Comparison of Radome Material Properties

Property	GD-1	Pyroceram	Si_3N_4
Strength at 25°C (ksi (MPa))	38 (260)	30 (210)	120 (830)
Elastic modulus (psi (GPa))	34×10^6 (230)	16×10^6 (110)	44×10^6 (300)
Knoop hardness	1300	620	2200
Density (g/cm^3)	3.02	2.6	3.2
Maximum use temperature (°C)	1300	1100	1500
Thermal expansion at 1000°C	4.1 × 10–6	6.6×10^{-6}	4.3×10^{-6}
Thermal conductivity (W/(m·K))	16	4	22
Thermal shock (figure of merit, $\sigma\kappa/E\alpha$)	9940	2000	27000
Dielectric constant at 1000°C	7.0–7.7	5.5	7.96
Loss tangent at 1000°C	0.003	0.03	0.013

Dolapix in Si_3N_4 suspensions had been demonstrated in an earlier study.[3]

Additional defoamers—Surfynol 104E (Air Products Inc., Allentown, Pa.) and Dapro 1139 (Daniel Products Co., Jersey City, N.J.)—were required to prevent and eliminate foaming during mixing and deairing. These were added to the mill and to the deairing chamber.

Gelcasting Initiator

The initiator system ammonium persulfate (APS) with tetra-methylethylene diamine (TEMED) was used to initiate free-radical polymerization in the gelcasting system. Addition of the standard 10 wt% APS solution to the slurry caused localized coagulation in the slurry, which caused the formation of clumps in the slurry. The pH of the APS solution as-mixed was ~2. It was hypothesized that the APS solution shifted the pH of the slurry to lower pH values and caused localized coagulation because of pH-induced flocculation. To mitigate this problem, the pH of the APS was adjusted to pH 9 before it was added to the slurry. This effectively prevented coagulation.

Table II. Raw Materials Selection for GD-1

Composition	Slip cast GD-1 (1985)	Gelcast GD-1 (1995)
Si_3N_4	Cerac	Ube E-5
Al_2O_3	Cerac	RC-HP-DBM
AlN	Cerac	ART-WR100
Y_2O_3	Alfa-Aesar	Molycorp
SiO_2	Alfa-Aesar	Alfa-Aesar

Large-Scale Processing

Each radome required ~4 kg of ceramic to fill the mold, which translated to ~5 L of suspension at 50 vol% solids. Mixing was accomplished in a 10 L polyethylene mill using ~2 kg of Si_3N_4 balls (1 cm diameter). All of the water, half of the dispersant and half of the Si_3N_4 powder were added to the mill and mixed at high speed for 4 h to disperse the Si_3N_4. Additional Si_3N_4 was added to the mill along with additional dispersant in the ratios 1:4, 1:8, 1:16 and 1:16 until all of the Si_3N_4 had been added and dispersed.

For each of the succeeding additions of Si_3N_4, a period of slow rolling was required to wet out and disperse the powder. This was required because the slurry became dilatant after each aliquot of Si_3N_4 was added, and slow rolling was the only way to incorporate the new powder into the existing slurry. Typically, the mill was slow rolled for 0.5–2 h (2–5 rpm) to wet out the new powder. Then the speed of the mill was slowly increased to its maximum fast-rolling speed (~100 rpm) over the course of 1–2 h. The mill was kept at the fast speed for an additional 2 h before the next addition of powder was made. Once all of the Si_3N_4 was well dispersed, the Al_2O_3, Y_2O_3 and SiO_2 were added. These materials were relatively easy to disperse. The last component added was the AlNWR100. The Emphos 1361 dispersant and the Foamaster VF defoamer were dissolved in the slurry; the AlN then was added and mixed for ~2 h, again following the procedure of slow rolling followed by faster rolling.

Once the slurry was mixed, it was deaired. Additional defoamers were added. Deairing was accomplished in a 40 L container

within a vacuum chamber. The large deairing container was required, because the slurry typically increased in volume by 5–6 times during deairing (up to 30 L) before the foam broke.

After the slurry was deaired, it was chilled to 5°C. This was done to ensure sufficient working time for the large volume of slurry. To ensure that the part could be gelled at ambient temperature, the initiator concentration was doubled relative to what was normally used for Si_3N_4-based gelcasting systems. However, because such a large volume of slurry was required to cast the radome, significantly more working time than normal also was required, which was in conflict with the shorter working time induced by the higher initiator concentration.

It was estimated that at least 20 min was needed to mix the initiator and catalyst with the slurry, to deair the slurry after initiator addition to remove bubbles and dissolved oxygen, to screen the slurry after deairing to remove coagulated clumps and dried flakes, and to cast the slurry into the mold. This conflict was resolved by chilling the suspension to ~5°C before adding the initiator. This provided >1 h of working time.

Casting

Casting the part was another adventure in gelcasting development. The mold for the radome weighed ~350 lb (160 kg) and, therefore, could not be easily moved. The mandrel weighed ~60 lb (27 kg) and was inserted after the slurry was poured into the mold cavity. The mold cavity was filled with a gravity feed system using an 8 L plastic reservoir with a plastic tube that connected to the bottom of the reservoir. This system allowed the slurry to be conveyed to the bottom of the mold, which prevented entrapping air bubbles in the casting.

After all of the slurry was transferred to the mold cavity, the mandrel was lowered into the slurry using a pulley system. The mandrel was secured in place using alignment pins and hold-down screws. The part was allowed to gel for ~2 h at ambient temperature. Then the mandrel was withdrawn using jack screws to break the mandrel away from the part. The pulley system then was used to fully withdraw the mandrel from the part.

Drying

Perhaps the biggest challenge of the project was drying the radome uniformly. The radome was in the shape of a thin-walled ogive or bullet-shaped cone. The as-gelled stiffness of the radome was far too low to hold its shape if it were to be taken out of the mold immediately after gelation. Therefore, the radome had to be partially dried in the mold. The challenge was to dry all regions of the radome at the same rate. Unfortunately, the nose of the radome invariably dried slower than the body. Because the tip was weak and pliable, it invariably cracked or broke off when the radome was removed from the mold (Fig. 3).

Several engineering approaches were attempted to solve these problems.

Fig. 3. Radome tip dried much slower than the body during air drying.

• The radome was dried slowly for 4 d by covering the open end with wet towels. The tip still dried much more slowly than the body.
• An air lance was lowered into the radome and dry air was directed at the tip of the radome. Moisture was carried away as the forced air was swept out of the mold. Even with the open end of the radome covered with plastic to prevent evaporation by diffusion and natural convection, the tip still dried much slower than the body of the radome.
• A temperature gradient was imposed on the mold using the heating channels included in the mold walls. Even with a temperature gradient of 20°C (30°C at the tip and 10°C at the open end), the tip still dried too slowly relative to the body of the radome to prevent cracking.

All of these approaches were handicapped because the air in the narrow tip region of the radome rapidly became saturated with water vapor, which significantly decreased the rate of drying in that region.

The drying problem was finally solved by applying a radically different drying approach. Instead of conducting the initial, in-mold drying of the radome using air, a liquid desiccant was used.[4] After the mandrel was removed from the mold, the mold was filled with poly(ethylene glycol) 400 (PEG400). The osmotic stress in the PEG400 was significantly higher than the osmotic stress in the gelcast gel. Therefore, water was pulled out of the gelled part and into the PEG400. Because the PEG400 was a liquid, it had access to all of the surfaces of the radome, including the tip. Also, the chemical potential for water to move from the gel into the PEG400 was quite high and was not limited by saturation effects, as had been the air-drying approaches.

After 1.5 h, the radome had dried as much as it would under the influence of the liquid desiccant. The PEG400 was siphoned out of the mold. At this point, the radome was uniformly leather hard from base to tip and was strong and stiff enough to be safely removed from the mold. After the radome was removed from the mold, it was rinsed in cold water to remove excess PEG400, covered with towels, and allowed to air dry slowly over night. The next day the radome was uncovered, and it was dried further at ambient conditions (~22°C and 50% RH) for another 24 h. Final drying was accomplished at 50°C in a convection oven. It was essential to remove as much water as possible before the radome was finish dried at 50°C to prevent reaction of AlN with water.

Thermal Processing

To remove the polymer binder, the green body was fired in air to 500°C before going to higher temperatures for densification. This temperature was high enough to remove all of the organics from the body, but no so high as to significantly oxidize the Si_3N_4 or AlN powders. Final densification was accomplished at 1650°C in nitrogen at ambient pressure.

Because GD-1 sinters by a liquid-phase mechanism, it becomes plastic during sintering. This property was used to advantage to define the final shape of the radome. The parts were fired conformally on a graphite mandrel, which defined the inner surface of the radome and resulted in a close to net shape part. The dimensions and positioning of the mandrel were such that the thermal expansion of the graphite and shrinkage of the dome produced the desired contour and size upon completing the thermal treatment.

Densification of the radome in the high-temperature step typically involved a uniform dimensional change of ~19%, such that the overall amount of shrinkage from the as-cast radome to the final product was only ~22% (i.e., the as-cast dimension was 1.22 times larger than the final dimension). Once the high-temperature firing was completed, the radome was removed from the mandrel and examined for dimensional tolerance. Although some machining was necessary to obtain the required dimensions, the results indicated that this step could be virtually eliminated with further development.

Full-size SiAlON radomes were fabricated using aqueous gelcasting. The keys to success included a water-resistant AlN powder that enabled the use an aqueous gelcasting system, mixing procedures that allowed achievement of high slurry density and liquid desiccant drying that made initial drying uniform, especially in the tip region. ■

Editor's Note:

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References

[1]R.F. Lowell, "Development of SiAlON for Single-Frequency and Broadband Radome Applications"; pp. 2-1-1–2-1-8 in *Proceedings of the 1st DoD Electromag Windows Symposium*, Vol. 1, 1985.

[2]K.W. Kirby, A. Jankiewicz, M.A. Janney, C.A. Walls and D.M. Kupp, "Gelcasting of GD-1 Ceramic Radomes"; pp. 287–99 in *Proceedings of the 8th DoD Electromag Windows Symposium*, 2000.

[3]M.A. Janney, O.O. Omatete, C.A. Walls, S.D. Nunn, R.J. Ogle and G. Westmoreland, "Development of Low-Toxicity Gelcasting Systems," *J. Am. Ceram. Soc.*, **81** [3] 581–91 (1998).

[4]M.A. Janney and J.O. Kiggans Jr., "Method of Drying Articles," U.S. Pat. No. 5 885 493, Mar. 23, 1999.